

| X—H···O | X—H | X···O | H···O | X—H···O |
|-----------------------------------|----------|-----------|----------|---------|
| N(11)—H(11)···O(1) ⁱ | 0.91 (4) | 2.884 (4) | 2.06 (5) | 150 (3) |
| N(11)—H(11)···O(2) ⁱ | 0.91 (4) | 2.984 (3) | 2.28 (3) | 135 (4) |
| N(17)—H(172)···O(1) ⁱ | 0.87 (4) | 2.917 (3) | 2.13 (3) | 149 (4) |
| N(17)—H(171)···O(2) ⁱⁱ | 0.79 (4) | 2.976 (3) | 2.21 (4) | 164 (4) |
| C(16)—H(16)···O(2) ⁱ | 0.98 (3) | 3.167 (4) | 2.56 (4) | 121 (3) |

Symmetry codes: (i) $-1 + x, y, z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

The densities of the compounds were measured by flotation in a $\text{CHBr}_3/n\text{-C}_6\text{H}_{14}$ mixture. Intensity data were corrected for Lorentz and polarization effects. Only a unique data set was collected. The structure was solved by Patterson methods and subsequent Fourier synthesis maps. The data refined with isotropic displacement parameters were corrected for absorption. A weighting scheme of type $w = w_1, w_2$ with $w_1 = k_1/(a + b|F_o|)^2$ and $w_2 = k_2/(c + d\sin\theta/\lambda + e\sin^2\theta/\lambda)$ was used to obtain flat dependence in $\langle w\Delta^2 F \rangle$ versus $\langle F_o \rangle$ and versus $\langle \sin\theta/\lambda \rangle$ (PESOS; Martínez-Ripoll & Cano, 1975). The coefficients used were $k_1 = 0.403$; $k_2 = 0.792$; $a = 1.369$, $b = -0.518$ for $|F_o| \leq 1.15$; $a = 0.766$, $b = -0.098$ for $1.15 < |F_o| \leq 3.07$; $a = 0.463$, $b = -0.026$ for $3.07 < |F_o| \leq 5.37$; $a = 0.188$, $b = 0.031$ for $5.37 < |F_o| \leq 21.58$; $a = -0.143$, $b = 0.050$ for $|F_o| > 21.58$; $c = 7.986$, $d = -35.299$, $e = 40.918$ for $\sin\theta/\lambda \leq 0.54$; $c = 2.106$, $d = -2.380$, $e = 0.000$ for $0.54 < \sin\theta/\lambda \leq 0.61$; $c = -5.201$, $d = 9.467$, $e = 0.000$ for $0.61 < \sin\theta/\lambda \leq 0.73$; $c = 0.752$, $d = -0.906$, $e = 0.746$ for $\sin\theta/\lambda > 0.73$. The non-H atoms were refined anisotropically. All H atoms were clearly visible in a difference Fourier synthesis and were refined isotropically. Most calculations were carried out using the XRAY76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) running on a MicroVAX II computer.

We are grateful for financial assistance from UPV/EHU (Grant No. 169.310-E180/91).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55686 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1013]

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Acta Cryst. (1993). **C49**, 587–589

Chlorobis(*N*-phenylsalicylideneaminato-*O,N*)manganese(III): a Manganese Schiff-Base Complex Derived by an Electrochemical Route

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(Received 21 September 1992; accepted 22 October 1992)

Abstract

The five-coordinate manganese cation is sited at the centre of an approximate trigonal bipyramid. Distortions involving, primarily, the axial N atom [N—Mn—N 169.41(9), Cl—Mn—N 98.13(7), 91.57(8)°] accommodate a ligand bite of less than 90° [N—Mn—O 86.8(1), 86.5(1)°] and a bulky equatorial Cl atom [Mn—Cl 2.235(1) Å].

Comment

The chemistry of manganese has attracted considerable attention recently as a result of its important role in biological processes such as photosynthesis (Ashmaw, McAuliffe, Parish & Tames, 1985). This interest has led to structural investigations of several penta-coordinate manganese(III) Schiff-base complexes including [Mn(acen)Cl], acen = *N,N'*-ethylenebis(acetylacetone imine), (Boucher & Day, 1977), [Mn(salen)Cl], salen = *N,N'*-ethylenebis(salicylaldiminato), (Pecoraro & Butler, 1986), [Mn(salen)(*p*-nitrobenzenethiolato)] (Gohdes & Armstrong, 1988), {Mn(salen)[2-(3-oxobut-2-enyl)phenolate]} (Li & Pecoraro, 1989) and [Mn(tetram-salen)Cl] (Oki & Hodgson, 1990). Unlike the title molecule, where the absence of an *N,N'* ethyl linkage

has facilitated a trigonal bipyramidal configuration, all the above complexes are square pyramids. The Mn—O bond lengths [1.866(2) and 1.858(2) Å] are unaffected by this change in geometry but the Mn—N bonds [2.193(2) and 2.158(2) Å] fall outside the range defined by the above complexes (1.970–2.010 Å). A significant reduction is also seen in the Mn—Cl bond length which at 2.235(1) Å is considerably shorter than in [Mn(acen)Cl], [Mn(salen)Cl] and [Mn(tetramesalen)Cl] [2.381(1), 2.461(1) and 2.391(4) Å, respectively]. The Schiff-base C=N bond lengths [average 1.294(3) Å] agree with a value of 1.30 Å proposed by Brown, Towns & Trefonas (1970) and the C—O bonds [average 1.322(3) Å] are intermediate between single and double bonds (Berthier & Serre, 1966). The shrinkage of the phenolate C—C bonds (which are most distant from the metal) is in accordance with observations made by Lin-gafelter & Braun (1966).

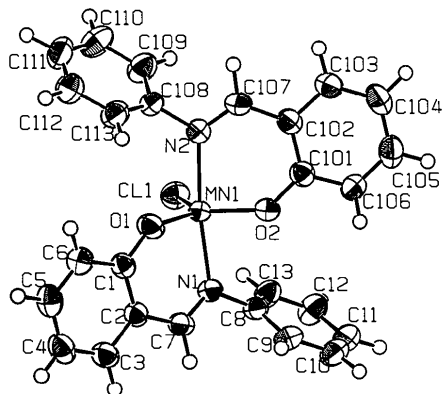


Fig. 1. View of the title molecule showing atomic numbering scheme drawn using ORTEP II (Johnson, 1976).

Experimental

Crystal data

[Mn(C₁₃H₁₀NO)₂Cl]

$M_r = 482.85$

Triclinic

$P\bar{1}$

$a = 9.688(3) \text{ \AA}$

$b = 10.669(3) \text{ \AA}$

$c = 12.447(5) \text{ \AA}$

$\alpha = 69.62(2)^\circ$

$\beta = 67.58(2)^\circ$

$\gamma = 78.86(4)^\circ$

$V = 1112(1) \text{ \AA}^3$

$Z = 2$

$D_x = 1.442 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.7107 \text{ \AA}$

Cell parameters from 20 reflections

$\theta = 15.42\text{--}17.36^\circ$

$\mu = 0.716 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Plate

$0.25 \times 0.25 \times 0.10 \text{ mm}$

Black

Data collection

CAD-4 diffractometer

$\omega/2\theta$ scans

$R_{\text{int}} = 0.016$

$\theta_{\text{max}} = 25.0^\circ$

Absorption correction:

azimuthal scans showed

correction not needed

$T_{\text{min}} = 0.95$, $T_{\text{max}} = 1.0$

3991 measured reflections

3919 independent reflections

2874 observed reflections

$[I > 2\sigma(I)]$

$h = 0 \rightarrow 11$

$k = -12 \rightarrow 12$

$l = -14 \rightarrow 14$

3 standard reflections

monitored every 150

reflections

intensity variation: not

significant

Refinement

Refinement on F

Final $R = 0.04$

$wR = 0.025$

$S = 2.08$

2874 reflections

370 parameters

All H-atom parameters re-

efined

Weighting scheme based on

measured e.s.d.'s

$(\Delta/\sigma)_{\text{max}} = 0.02$

$\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$

Extinction correction:

Zachariasen type 2 Gaus-

sian isotropic

Extinction coefficient:

8.08045

Atomic scattering factors

from *International Tables*

for X-ray Crystallography

(1974, Vol. IV)

Data collection: Enraf-Nonius CAD-4 diffractometer control.

Cell refinement: Enraf-Nonius diffractometer control. Data

reduction: *TEXSAN: PROCESS* (Molecular Structure Corpo-

ration, 1985). Program(s) used to solve structure: *MITHRIL*

(Gilmore, 1984). Program(s) used to refine structure: *TEXSAN:*

LS. Molecular graphics: *TEXSAN: PLUTO, ORTEP*. Software

used to prepare material for publication: *TEXSAN: FINISH*.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

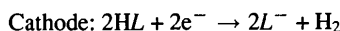
$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

| | x | y | z | U_{eq} |
|------|-------------|-------------|-------------|-----------------|
| Mn1 | 0.29542 (5) | 0.69994 (4) | 0.22040 (4) | 0.0340 |
| Cl1 | 0.07414 (9) | 0.68820 (8) | 0.37080 (8) | 0.0531 |
| O1 | 0.4695 (2) | 0.6789 (2) | 0.2575 (2) | 0.0481 |
| O2 | 0.3029 (2) | 0.7292 (2) | 0.0622 (2) | 0.0498 |
| N1 | 0.3342 (3) | 0.4924 (2) | 0.2298 (2) | 0.0387 |
| N2 | 0.2840 (3) | 0.9151 (2) | 0.1766 (2) | 0.0409 |
| C1 | 0.5457 (3) | 0.5747 (3) | 0.3099 (3) | 0.0400 |
| C2 | 0.5290 (3) | 0.4419 (3) | 0.3198 (3) | 0.0396 |
| C3 | 0.6123 (4) | 0.3356 (3) | 0.3773 (3) | 0.0487 |
| C4 | 0.7072 (4) | 0.3588 (4) | 0.4255 (3) | 0.0558 |
| C5 | 0.7263 (4) | 0.4899 (4) | 0.4128 (3) | 0.0525 |
| C6 | 0.6478 (4) | 0.5949 (4) | 0.3561 (3) | 0.0473 |
| C7 | 0.4321 (3) | 0.4095 (3) | 0.2716 (3) | 0.0426 |
| C8 | 0.2600 (3) | 0.4425 (3) | 0.1733 (3) | 0.0398 |
| C9 | 0.3437 (4) | 0.3895 (3) | 0.0794 (3) | 0.0460 |
| C10 | 0.2708 (4) | 0.3503 (3) | 0.0205 (3) | 0.0531 |
| C11 | 0.1163 (4) | 0.3617 (3) | 0.0577 (3) | 0.0563 |
| C12 | 0.0354 (4) | 0.4117 (4) | 0.1532 (3) | 0.0585 |
| C13 | 0.1048 (4) | 0.4534 (3) | 0.2117 (3) | 0.0529 |
| C101 | 0.2553 (3) | 0.8289 (3) | -0.0171 (3) | 0.0419 |
| C102 | 0.2284 (3) | 0.9613 (3) | -0.0097 (3) | 0.0420 |
| C103 | 0.1796 (4) | 1.0640 (3) | -0.0978 (3) | 0.0536 |
| C104 | 0.1590 (4) | 1.0374 (4) | -0.1905 (3) | 0.0575 |
| C105 | 0.1857 (4) | 0.9056 (4) | -0.1972 (3) | 0.0571 |
| C106 | 0.2339 (4) | 0.8055 (4) | -0.1133 (3) | 0.0501 |
| C107 | 0.2452 (3) | 0.9956 (3) | 0.0865 (3) | 0.0446 |
| C108 | 0.2849 (4) | 0.9739 (3) | 0.2640 (3) | 0.0420 |
| C109 | 0.1592 (4) | 1.0429 (4) | 0.3214 (3) | 0.0588 |
| C110 | 0.1600 (5) | 1.0984 (4) | 0.4068 (4) | 0.0688 |
| C111 | 0.2876 (5) | 1.0826 (4) | 0.4357 (3) | 0.0649 |
| C112 | 0.4131 (5) | 1.0144 (4) | 0.3776 (4) | 0.0622 |
| C113 | 0.4127 (4) | 0.9591 (3) | 0.2923 (3) | 0.0532 |

Table 2. Geometric parameters (Å, °)

| | | | |
|------------|------------|-----------|------------|
| Mn1—Cl1 | 2.235 (1) | O2—C101 | 1.321 (4) |
| Mn1—O1 | 1.866 (3) | N1—C7 | 1.298 (4) |
| Mn1—O2 | 1.858 (3) | N1—C8 | 1.444 (5) |
| Mn1—N1 | 2.143 (3) | N2—C107 | 1.289 (4) |
| Mn1—N2 | 2.158 (3) | N2—C108 | 1.436 (5) |
| O1—C1 | 1.323 (4) | | |
| Cl1—Mn1—O1 | 118.81 (8) | O1—Mn1—N1 | 86.8 (1) |
| Cl1—Mn1—O2 | 119.74 (8) | O1—Mn1—N2 | 92.3 (1) |
| Cl1—Mn1—N1 | 98.13 (7) | O2—Mn1—N1 | 85.0 (1) |
| Cl1—Mn1—N2 | 91.57 (8) | O2—Mn1—N2 | 86.5 (1) |
| O1—Mn1—O2 | 121.44 (9) | N1—Mn1—N2 | 169.41 (9) |

The Schiff base, *N*-salicyldenephylamine (HL), was prepared by refluxing equimolar amounts of salicylaldehyde and aniline in chloroform until the expected amount of water was collected in a Dean–Stark trap. After checking its purity using IR and ¹H NMR spectra, the Schiff base was used to prepare [MnL₂phen] by an electrochemical method similar to that described by Habeeb, Tuck & Walters (1978). The electrochemical oxidation of manganese was carried out in a 100 ml 'tall-form' beaker with a solution of 0.27 g of HL (1.37 mmol), 0.121 g of 1,10-phenanthroline (phen) (6.72 mmol) and 10 mg of tetraethylammonium perchlorate in 50 ml of acetonitrile by applying a voltage of 10 V and a current of 20 mA for 1.83 h. The cell can be summarized as Pt⁻/CH₃CN + HL/Mn⁺. The reaction mixture was subsequently filtered to remove metal particles and the filtrate concentrated by low-pressure evaporation at room temperature. The solid, [MnL₂phen], thus formed was washed with acetonitrile and dried. Analysis: found C, 72.7; H, 4.4; N, 8.9. Calculated for [Mn(C₁₃H₁₀NO)₂(C₁₂H₈N₂)]: C, 72.7; H, 4.5; N, 8.9. The electrochemical efficiency of 0.56 mol Faraday⁻¹ derived from the volume of hydrogen evolved at the cathode is compatible with the following reaction scheme:



Tetrachloroferrate-ferrocenium was prepared by the addition of a solution of ferrocene (0.2 mol) in 600 ml anhydrous ethyl ether to a suspension of anhydrous FeCl₃ (0.4 mol) in 300 ml of the same solvent. After stirring, a blue-green precipitate formed; this was filtrated and dried *in vacuo*. [MnL₂Cl] was obtained by the chemical oxidation of [MnL₂phen] with Cp₂Fe⁺.FeCl₄⁻. A solution of Cp₂Fe⁺.FeCl₄⁻ (0.176 g, 0.459 mmol) in acetonitrile was added to a suspension of [MnL₂phen] (0.288, 0.459 mmol) in the same solvent. The reaction mixture was stirred until a clear solution was obtained, which was reduced in volume by 75% followed by the addition of diethyl ether to precipitate a solid. The solid was filtered and the remaining solution concentrated by slow evaporation at room temperature to give X-ray quality crystals of [MnL₂Cl]. Analysis: found C, 65.3; H, 4.0; N, 5.9; Calculated for [Mn(C₁₃H₁₀NO)₂Cl]: C, 64.7; H, 4.1; N, 5.8.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55764 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1035]

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cis-Dichloro(di-*n*-butyl sulfide)(tri-*n*-butylphosphine)platinum(II)

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(Received 6 May 1992; accepted 1 October 1992)

Abstract

cis-Dichloro(di-*n*-butyl sulfide)(tri-*n*-butylphosphine)-platinum(II) was prepared by reacting *sym-trans*-[Pt₂Cl₄(PBU₃)₂] with two equivalents of di-*n*-butyl sulfide in dichloromethane solution. The complex has a square-planar structure with the two neutral ligands in *cis* positions.

Comment

We are interested in simple platinum compounds containing phosphine and sulfide ligands as models

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